



In situ growth of Ag-reduced graphene oxide-carbon nanotube on indium tin oxide and its application for electrochemical sensing



Yong Zhang^{a,b}, Ziyang Wang^a, Sen Liu^{a,**}, Tong Zhang^{a,b,*}

^a State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun, PR China

^b State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, PR China

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ABSTRACT

Herein, a two-step electrodeposition method was carried out for in situ growth of Ag metal-reduced graphene oxide-carbon nanotube on indium tin oxide (Ag-rGO-CNT/ITO). Firstly, rGO-CNT hybrids have been synthesized on ITO electrode by electrodeposition of GO-CNT dispersion, and then, Ag metal has been deposited on the surface of rGO-CNT/ITO by the electrodeposition method. Combining unique properties of rGO-CNT hybrids and excellent catalytic activity of Ag metal, Ag-rGO-CNT/ITO exhibits good catalytic activity for electrocatalytic reduction of hydrogen peroxide (H₂O₂). The non-enzymatic H₂O₂ sensor based on Ag-rGO-CNT/ITO electrode shows the linear detection range about 0.05–1.40 mM (R = 0.999), and the detection limit is estimated to be 1.32 μM at a signal-to-noise ratio of 3. Furthermore, the Ag-rGO-CNT/ITO electrode exhibits good anti-interference capability, compared to other interferences such as ascorbic acid, dopamine, uric acid, NaNO₃, NaNO₂ and glucose.

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1. Introduction

During the past few years, considerable attention has been focused on determination of hydrogen peroxide (H₂O₂) in trace levels in biological and various water samples. It is obvious that H₂O₂ is not only an important intermediate species in food, pharmaceutical and environmental analysis, but also considered as the mediators of the cellular pathology in association with aging and severe human diseases such as cancers and cardiovascular disorders [1–3]. Compared with other detection techniques, electrochemical technique has been proven to be an inexpensive and effective strategy due to its advantages of intrinsic simplicity, high sensitivity and high selectivity. Meanwhile, the electrochemical methods based on non-enzymatic sensors avoid the possibility of protein denaturing, providing a promising method for fabrication of highly stable electrochemical sensors [4–6].

It is well known that Ag-based materials exhibit good electrocatalytic activity toward reduction of H₂O₂, and they have been widely developed for fabrication of non-enzymatic H₂O₂ sensors [7,8]. For example, pure Ag-based materials with various size or structure have been developed for construction of H₂O₂ sensors

[9–11]. Although enhanced sensing performances have been successfully achieved compared to other sensing materials, the stabilizing agents (such as polymers, surfactants) always exist in the final samples, which would prevent the electrons transfer rate, leading to poor sensing performances [12,13]. Additionally, the particle size is another important factor for improvement of sensing performances [14]. The Ag-based materials with the size more than few micrometer exhibit low specific surface area and poor dispersing ability, while Ag-materials with small size (smaller than several nanometer) tend to form compact film on the surface of electrode.

To overcome the problems, deposition of Ag metal onto support materials has been proven as an effective method to obtain enhanced sensing performances. Considerable efforts have recently been focused on designing various support materials to enhance the performance of Ag metal for H₂O₂ detection. Among them, reduced graphene oxide (rGO) possesses unique advantages of high surface area, high carrier mobility, good chemical stability, low-cost, as well as easy modification [15–18]. Up to now, a variety of Ag nanomaterials-supported on rGO (Ag/rGO) hybrids have been successfully developed for fabrication of H₂O₂ sensor with enhanced sensing performances, compared to pure Ag-based nanomaterials [19,20]. It is obviously seen that the sensing performances have been improved obviously by introduction of rGO. However, there are still some problems should be overcome from the view of materials structure. For example, a compact film is

* Corresponding author at: State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun, PR China.

** Corresponding author.

E-mail addresses: liusen@jlu.edu.cn (S. Liu), zhangtong@jlu.edu.cn (T. Zhang).

obtained after volatilizing the solvent of the Ag/rGO hybrids due to the strong π - π interactions between rGO-based materials, resulting in hiding parts of Ag (active site) in the matrix of rGO [21,22]. Thus, the sensing performances could be further enhanced by exposure of more active sites of sensing materials into electrolyte solution.

It is deduced that introduction of porous structure in the Ag/rGO hybrids should be an effective strategy for enhancing the sensing performances preventing from the aggregates of rGO-based materials. Recent researches have shown that rGO-carbon nanotube (rGO-CNT) composites have attracted substantial research interest due to their unique porous structure and electron transfer property [23,24]. Recently, Lorestani et al. have prepared Ag nanoparticle-CNT-rGO composite by one-step hydrothermal method for detection of H_2O_2 [25]. Our group has synthesized Ag nanoparticles-rGO-CNT hybrids by alkaline-assisted wet-chemical method for electrochemical H_2O_2 detection [26]. Although enhanced sensing performances are obtained by introduction of CNT into rGO matrix, these systems exhibit obvious shortcomings for further overcome. For example, it is noted that these Ag-rGO-CNT hybrids are difficult to form uniform and stable aqueous dispersion due to the surface hydrophobicity of rGO and CNT. Normally, the preparation of modified electrode for electrochemical detection was performed by drop-coating of aqueous dispersion of functional materials on the surface of working electrode. When the uneven dispersion of functional materials is dropped on working electrode, it is difficult to form a stable film comprising of functional materials on the surface of working electrode, thus leading to poor stability and reproducibility of modified electrode. This problem also appears on other rGO-based and rGO-CNT-based materials for the application of electrocatalysts and electrochemical detection. Fortunately, the addition of auxiliary materials such as Nafion into the functional materials could improve the dispersing ability of functional materials in aqueous dispersion, which could aid to the film-forming of functional materials on working electrode [27,28]. However, addition of auxiliary materials in the functional materials certainly will influence the electrochemical activity of functional materials. Hence, a novel synthetic method for direct forming stable film of Ag-rGO-CNT hybrids is highly required.

More recently, electrodeposition method has been developed for preparation of rGO-modified electrode for electrochemical sensing, providing a new and efficient method for preparation of rGO-based sensing film [29,30]. Our previous work showed the electrodeposition synthesis of rGO-CNT hybrids. Furthermore, this rGO-CNT film exhibited excellent electrochemical activity and good performances for simultaneous electrochemical detection of ascorbic acid, dopamine and uric acid [31]. Notably, the electrodeposition method is a simple and environmental friendly method, which can not only support to form stable film of rGO-based materials on the surface of working electrode but also has an advantage of outstanding electronic conductivity between rGO-based materials and working electrode, compared to the method for drop coating of functional materials on working electrodes. Therefore, the electrodeposition preparation of Ag-rGO-modified electrodes for electrochemical sensing have been proposed [32,33].

In addition, it is well known that indium tin oxide (ITO) electrode can be used as an electrochemical sensing platform due to its wide potential window and stable electrochemical properties [34]. Furthermore, compared with glassy carbon electrode (GCE), ITO is a cost-effective material and more suitable for mass production and practical application, which is accustomed to be used as the substrate for fabricating disposable sensors, such as H_2O_2 [35], glucose [36] and hydrazine [37] sensors. To the best of our knowledge, however, preparation of Ag-rGO-CNT modified

electrode by the electrodeposition method for electrochemical sensing has never been reported so far.

In this paper, Ag metal-rGO-CNT modified ITO (Ag-rGO-CNT/ITO) electrode has been successfully synthesized by two-step electrodeposition method. The application of Ag-rGO-CNT/ITO electrode has been demonstrated for electrochemical detection of H_2O_2 , leading to a disposable and non-enzymatic H_2O_2 sensor. Moreover, the Ag-rGO-CNT/ITO electrode has also been proven to be effective for selective determination of H_2O_2 .

2. Experimental

2.1. Materials and reagents

Graphite powder and dopamine (DA) were purchased from Aladin Ltd. (Shanghai, China). Multi-walled carbon nanotube (MWCNT) was purchased from Shenzhen Nanotech Port. NaNO_3 , NaNO_2 , KNO_3 , KMnO_4 , $\text{NaH}_2\text{PO}_4 \cdot 9\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 9\text{H}_2\text{O}$, ascorbic acid (AA), uric acid (UA), and glucose were purchased from Beijing Chemical Works (Beijing, China). AgNO_3 (99.8%) was obtained from Shanghai Chemical Corp (Shanghai, China). Silicone rubber was purchased from Zhonghao Chenguang Research Institute of Chemical Industry (Sichuan, China). The solvents including H_2SO_4 (98%) and H_2O_2 (30 wt%) were supplied by Beijing Chemical Works (Beijing, China). All reagents were used directly without further purification. The deionized water used throughout all experiments was purified through a Millipore system. Phosphate buffered saline (PBS) was prepared by mixing stock solutions of NaH_2PO_4 and Na_2HPO_4 and a fresh solution of H_2O_2 was prepared daily.

2.2. Preparation of Ag-rGO-CNT/ITO electrode

GO was prepared from natural graphite powder through a modified Hummers' method [38]. rGO-CNT/ITO electrode was prepared according to our previous established method [31]. In brief, an ITO conductive glass (6.0 cm \times 0.6 cm) was masked by silicone rubber. The electrolyte was prepared by ultrasonic dispersing 11.0 mg of CNT and 5.0 mg of GO into 5.0 mL of 0.2 M PBS (pH 6.5) for 2 h. A conventional three-electrode cell was used, including an ITO (geometric area = 0.3 cm²) as the working electrode, a Ag/AgCl electrode as the reference electrode, and platinum foil as the counter electrode. Cyclic voltammetry (CV) was performed by scanning between 0 and -1.0 V at a rate of 50 mV s⁻¹ with 10 potential cycles. Then the working electrode was rinsed with water and further processed by CV with 10 potential cycles in 0.2 M PBS solution (pH 6.5). (Scan range: 0 to -1.0 V; Scan rate: 50 mV s⁻¹)

The Ag-rGO-CNT/ITO was prepared by electrodeposition of Ag metal on the surface of rGO-CNT/ITO. The conventional three-electrode cell was used for preparation of Ag-rGO-CNT/ITO, where rGO-CNT/ITO, Ag/AgCl electrode and platinum foil were used as the working electrode, reference electrode, and counter electrode. Furthermore, electrolyte solution was obtained by addition of 40 μL of 0.5 M AgNO_3 into 5.0 mL of 0.1 M KNO_3 solution. The electrochemical deposition of Ag was performed by amperometry at -0.3 V for 3 min. The Ag-rGO-CNT/ITO was taken off and rinsed with water three times lightly for characterization and further use.

The rGO/ITO electrode was prepared by the similar method for preparation of rGO-CNT/ITO electrode in the absence of CNT. The Ag-rGO/ITO electrode was also prepared by the similar method for preparation of Ag-rGO-CNT/ITO electrode, where rGO/ITO was used as working electrode instead of rGO-CNT/ITO electrode.

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